

APPROACH TO THE IRON-CATALYZED FORMATION PROCESS OF N_2 FROM HETEROCYCLIC NITROGEN IN CARBON BY USE OF XRD AND XPS METHODS

Yasuhiro Ohshima, Ye Wang, Naoto Tsubouchi, and Yasuo Ohtsuka

Research Center for Organic Resources and Materials Chemistry

Institute for Chemical Reaction Science, Tohoku University

Katahira, Aoba-ku, Sendai 980-8577, JAPAN

KEYWORDS: Fuel nitrogen, iron catalyst, X-ray diffraction analysis

ABSTRACTS

PAN-derived carbon as a model of coal char has been heated in high purity He, and the catalysis of N_2 formation by precipitated iron has been investigated by means of TEM, XPS and XRD. Nanoscale iron particles are very active for this reaction at 600 – 1000°C. The XPS and XRD analyses after heat treatment reveal that nitrogen functionality does not change significantly but carbon crystallization takes place via the dissolution of iron into the carbon substrate. The *in situ* XRD measurements during heating show the formation of solid solution of iron and nitrogen (and carbon). The iron-catalyzed conversion of heterocyclic nitrogen to N_2 probably proceeds through formation of the solid solution and subsequent decomposition into N_2 .

INTRODUCTION

The nitrogen present in coal (coal-N) is emitted as NO_x and N_2O during combustion. The NO_x has been implicated in acid rain and photochemical smog. In conventional pulverized coal-fired plants, 75 – 95 % of the NO_x emitted originates from coal-N. The N_2O is known to be involved in the green house effect and the ozone layer depletion. The concentration of N_2O is much higher in fluidized bed combustion that can be operated at lower temperatures (< 1000°C) than in pulverized coal-fired boilers. The N_2O arises from coal-N alone. When coal is fed into a combustion chamber, the devolatilization (pyrolysis) first takes place. In this process, part of coal-N is released as tar-N, and the remainder is retained as char-N, some of the tar-N being subsequently decomposed into HCN and NH_3 [1,2]. All these nitrogen species are the precursors of NO_x and N_2O . If coal-N can be converted efficiently to N_2 upon devolatilization, the emissions of NO_x and N_2O can greatly be reduced during subsequent combustion.

The present authors' group has found that FeOOH precipitated on low rank coals can drastically catalyze conversion of coal-N to N_2 in the fluidized bed pyrolysis at $\geq 750^\circ\text{C}$ [3,4]. We have also shown that Fe-containing minerals in low rank coals, probably as ion-exchanged forms, can also promote N_2 formation in the fixed bed pyrolysis at almost the same temperature range as above [5,6]. Since N_2 formation occurs dominantly after complete release of volatile-N (tar-N, HCN, and NH_3), it is strongly suggested that the iron derived from Fe-containing minerals as well as FeOOH catalyzes conversion of char-N to N_2 . However, the detailed mechanism is not clear. The present work therefore focuses on making clear the Fe-catalyzed formation process of N_2 at solid phase by using PAN-derived carbon as a model of coal char.

EXPERIMENTAL

Pure carbon without any minerals was used in place of coal char in order to avoid their influences on N_2 formation. The carbon was prepared by carbonization of PAN for 30 min at 1000°C, followed by activation in 20 vol% O_2 at 500°C. The C, H and N contents in the carbon with size fraction of 44 – 74 μm were 79.3, 0.4 and 6.8 wt%, respectively, the BET surface area determined by N_2 adsorption being 480 m^2/g . Fine particles of FeOOH were precipitated onto the carbon from an aqueous solution of FeCl₃ by using $\text{Ca}(\text{OH})_2$ [7].

The carbon (180 mg) with or without 1.9 wt% Fe was heated with a fixed-bed quartz reactor in a

stream of high purity He ($> 99.9999\%$) at $10^{\circ}\text{C}/\text{min}$ up to 1000°C , and N_2 evolved was determined on line at 5 min intervals with a high speed micro GC. Detailed procedures have been described elsewhere [5]. The samples before and after heat treatment were characterized by TEM, XPS and XRD. The *in situ* XRD measurements were also made with Mn-filtered $\text{Fe-K}\alpha$ radiation during heating the Fe-loaded carbon under the same conditions as above.

RESULTS AND DISCUSSION

Formation of N_2 . Figure 1 shows the temperature-programmed profiles for N_2 formation. The iron remarkably promoted conversion to N_2 at $600 - 1000^{\circ}\text{C}$. The catalytic effect appeared at a lower temperature of around 600°C than observed with low rank coals [3,4], probably because of a lower heating rate in the present work. The rate of N_2 formation reached the maximal value at 800°C and then decreased. The rate at 800°C with $1.9\text{ wt}\%$ Fe was about 10 times that without catalyst. The presence of the iron almost doubled N_2 yield after 60 min soaking at 1000°C , the yield being 32 and 63 % without and with $1.9\text{ wt}\%$ Fe, respectively.

XPS spectra. The N 1s XPS spectra were measured to examine the change in nitrogen functionality upon heat treatment, and least-squares curve fitting of the spectra was performed using Gaussian peak shapes [8]. Pyrrolic-N ($398.7 \pm 0.1\text{ eV}$), and pyridinic-N ($400.3 \pm 0.1\text{ eV}$) were the main nitrogen forms in the original carbon before heat treatment. The ratio was almost unity, which was much lower than that observed for brown coal char after pyrolysis at 900°C [8]. When the carbon with $1.9\text{ wt}\%$ Fe was heated at $600 - 1000^{\circ}\text{C}$, the distribution of pyrrolic-N, pyridinic-N and quaternary-N ($401.4 \pm 0.1\text{ eV}$) was significantly unchanged. This suggests that N_2 evolves from these species at almost the same rate. On the other hand, the iron precipitated on brown coal is effective for preferential formation of N_2 from pyrrolic-N [8]. The difference may be related with a larger ratio of pyrrolic-N/pyridinic-N in the latter case.

TEM observations. The average size of iron particles at 600°C , that is, before the start of N_2 formation, was as fine as 15 nm. When the iron was precipitated onto PAN-derived carbon without O_2 -activation in the same manner as above, the average particle size was much larger (70 nm), and the iron was less active. The activation increased not only the surface area but also the amount of oxygen functional groups, which lead to the formation of the more highly dispersed iron on the activated carbon. The average size increased from the initial 15 nm to 23 nm after heat treatment at 1000°C . In the size distribution, most of iron particles were initially $\leq 20\text{ nm}$ in size, whereas more than half of them were $\geq 20\text{ nm}$ at 1000°C , and the iron with the size of 40 – 60 nm was also observed. These observations show that iron particles move within the carbon matrix, catalyze N_2 formation, and agglomerate in this process.

XRD measurements. Figure 2 shows the XRD profiles for Fe-bearing samples cooled to room temperature after heat treatment. At 600°C , the small peaks of magnetite (Fe_3O_4) and wustite (Fe_{1-x}O) were observed, which means the transformation of the initial form of FeOOH to these oxide forms. At 1000°C , the oxide species disappeared, and instead the XRD lines of metallic iron ($\alpha\text{-Fe}$) and cementite (Fe_3C) appeared. Not only the reduction to metallic iron but also the reaction of the iron with the carbon substrate took place between 600 and 1000°C . Figure 2 also provides information about carbon structures due to C(002) lines, which can be separated into amorphous and turbostratic carbon, denoted as A- and T-carbon respectively, by deconvolution. As the temperature increased, the proportion of T-carbon increased from 14 to 18 %. On the other hand, no significant change in C(002) lines was observed in the absence of the iron. The formation of cementite and T-carbon indicates that the iron first dissolves in the carbon substrate and subsequently catalyzes crystallization reactions [9]. It can readily be expected that the iron reacts with heterocyclic nitrogen forms in the carbon matrix.

Figure 3 shows the *in situ* XRD profiles during heating the carbon with $1.9\text{ wt}\%$ Fe. At 655°C , metallic iron ($\alpha\text{-Fe}$) was the dominant species, though the small peaks of wustite were also observed. Interestingly, the XRD lines of austenite, solid solution of $\gamma\text{-Fe}$ and nitrogen

(and/or carbon), existed as well. When the temperature was raised to 815 and 1025°C, the XRD intensities of this species increased with a corresponding decrease in the intensity of metallic iron, and austenite was the predominant form in this temperature region. When the sample heated at 1025°C was quenched to room temperature, metallic iron and cementite were formed, in harmony with the XRD profile given in Figure 2.

Mechanism. It should be noted that the catalysis of conversion to N_2 by iron (Figure 1) and the formation of austenite (Figure 3) occur at almost the same temperature range. According to phase diagrams of Fe-N and Fe-C [10], nitrogen can dissolve rapidly into iron at a lower temperature of about 590°C, compared with that (740°C) for carbon. The former temperature corresponded well to the onset of the Fe-catalyzed formation of N_2 . It is thus likely that the austenite observed at < 740°C is the solid solution of Fe and N, and that N_2 formation in this temperature range proceeds through the intermediate. The austenite may be transformed to iron nitrides (Fe_3N), which can readily be decomposed into N_2 because of thermal instability [8]. The austenite formed at $\geq 740^\circ\text{C}$ may be composed of Fe, N and C, and converted to Fe_3N_2C as well as Fe_3N . The decomposition of Fe_3N_2C into N_2 may involve carbon crystallization, that is, the formation of turbostratic carbon (Figure 2). The presence of such crystallized carbon might prevent iron particles from moving within the carbon matrix. As mentioned above, the TEM observations revealed that catalyst agglomeration took place in the process of N_2 formation. The lowering in both mobility and activity of iron particles may be responsible for the decreased rate of N_2 formation observed after 800°C (Figure 1).

CONCLUSIONS

Fine iron particles with the average size of 15 nm promote remarkably N_2 formation from PAN-derived carbon during heating in an inert gas at 600 – 1000°C. Catalyst agglomeration occurs in this process. The XPS spectra show that pyrrolic-N and pyridinic-N are the main forms, and that such nitrogen functionality is significantly unchanged upon heat treatment. The XRD analyses reveal the transformation of amorphous to turbostratic carbon, meaning the dissolution of the iron into the carbon substrate. Furthermore, the *in situ* XRD measurements during heating show the formation of austenite that is solid solution of iron and nitrogen (and carbon). It is likely that iron nanoparticles move in the carbon matrix and react with heterocyclic nitrogen to form the solid solution, which is subsequently decomposed into N_2 .

ACKNOWLEDGMENTS

The present work was supported in part by the Proposal-Based New Industry Creative Type Technical R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO), Japan. The authors acknowledge the assistance of Ms. Hazuki Satake in carrying out experiments.

REFERENCES

- 1 Davidson, R.M. In *Nitrogen in Coal*; IEAPER/08; IEA Coal Research: London, 1994.
- 2 Leppälähti, J.; Koljonen, T. *Fuel Processing Technology* **1995**, *43*, 1.
- 3 Ohtsuka, Y.; Mori, H.; Watanabe, T.; Asami, K. *Fuel* **1994**, *73*, 1093.
- 4 Mori, H.; Asami, K.; Ohtsuka, Y. *Energy Fuels* **1996**, *10*, 1022.
- 5 Wu, Z.; Ohtsuka, Y. *Energy Fuels* **1997**, *11*, 477.
- 6 Wu, Z.; Ohtsuka, Y. *Energy Fuels* **1997**, *11*, 902.
- 7 Ohtsuka, Y.; Asami, K. *Catalysis Today* **1997**, *39*, 111.
- 8 Ohtsuka, Y.; Watanabe, T.; Asami, K.; Mori, H. *Energy Fuels* **1998**, *12*, 1356.
- 9 Oya, A.; Marsh, H. J. *Mater. Sci.* **1982**, *17*, 309.
- 10 Massalski, T.B. In *Binary Alloy Phase Diagrams*; Vol. 2; ASM International: Ohio, 1990.

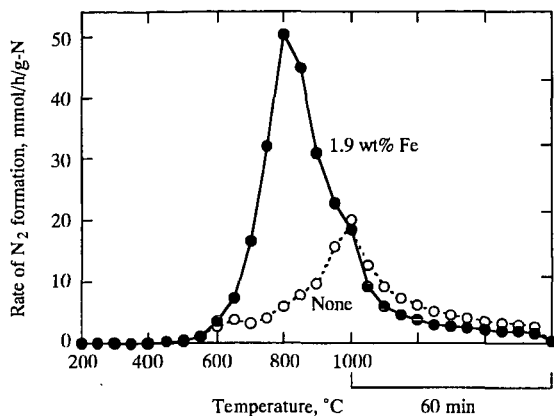


Figure 1 N_2 formation during temperature programmed heat treatment of PAN-derived carbon.

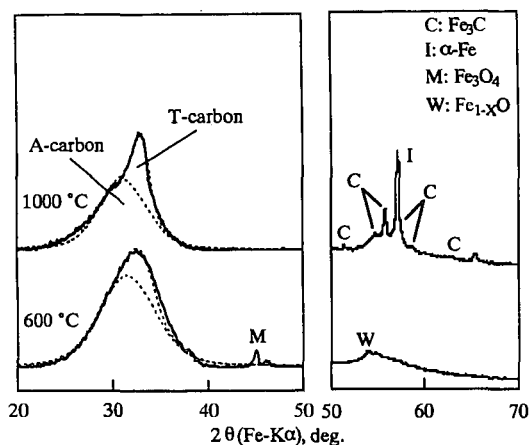


Figure 2 XRD results for Fe-bearing samples cooled to room temperature after heat treatment.

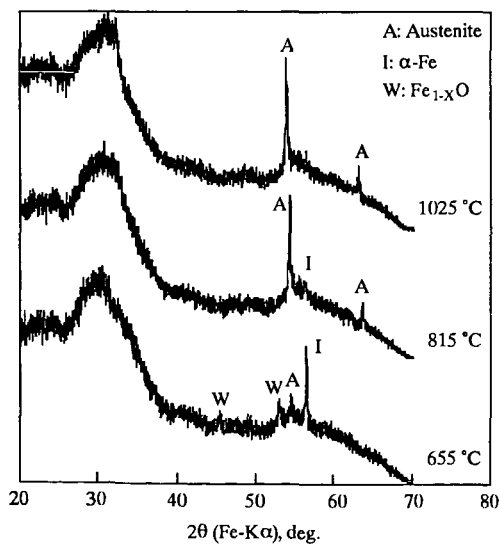


Figure 3 *In situ* XRD profiles during heating of Fe-bearing carbons.